PATENT SPECIFICATION

DRAWINGS ATTACHED

1,189,029

Date of Application (No. 38530/68) and filing Complete Specification: 12 Aug., 1968.

Application made in United States of America (No. 660,228) on 14 Aug., 1967.

Application made in United States of America (No. 685,770) on 27 Nov., 1967.

Complete Specification Published: 22 April, 1970.

Index at acceptance:—C3 R(22A, 22C6A1, 22C6X, 22C8P, 22C14A, 22C28X, 22C33B, 22C33X, 22D1A2, 22D2A2, 22L2CX, 22L5A, 22L5X, 22N1A)

International Classification:—C 08 g 41/00

COMPLETE SPECIFICATION

Oriented Polyamide Articles

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in oriented articles made from polyamide resin, and more particularly to a method and composition for improving physical properties of such articles.

Polyamide resin can be melt fabricated into an elongated shape such as that of a ribbon and thereafter longitudinally oriented to form useful articles such as power transmission belting and strapping, disclosed in U.S. Patent No. 2,999,764 to J. E. Rhoads, and British Patent No. 1,017,175 to Du Pont, respectively.

Unfortunately, as the degree of orientation of the polyamide ribbon increases, certain characteristics appear which may hamper its usefulness. For example, resistance to longitudinal splitting of the oriented article decreases, which may be deleterious to the resistance to delamination desired for use as power transmission belting. For strapping, a new technique for joining the strapping to itself has been developed, which is called friction welding. Friction welding is described in a publication by Signode Corporation, identified as SPD 360 7/66—10M—A and entitled "An Introduction To Tension Weld—The Process, The Tool, The Weld Itself". This method of joining strapping involves the rubbing together of overlapping ends of strapping while under tension, the ends being pressed together under sufficient pressure and for sufficient time to cause localized melting. This causes the molten areas of the strapping to weld the overlapping ends together. While such welding as applied to polyamide strapping does not significantly destroy its orientation, the strength of the weld is relatively low and impairs the strength-in-use to that extent.

The polyamide resins employed in the present invention are well-known articles of commerce, and generally have a molecular weight in excess of about 2000. The particular resin selected should be capable of sufficient orientation to provide strength required for the application involved. Representative polyamide resins include polyhexamethylene adipamide, polyhexamethylene sebacamide, polycaprolactam and copolymers thereof. The polyamide resins can include such additives as plasticizers, antioxidants, and other conventional additives, such as described in British Patent No. 1,017,175 (U.S. Patent No. 3,354,023).

It has been found in accord with the present invention that when a small amount of modifier resin (described herein) is incorporated into the polyamide resin to be used for forming an oriented article, the oriented article made therefrom exhibits improved friction weldability and resistance to longitudinal splitting, as compared to the same oriented article made of polyamide resin without the modifier resins of the present invention.

The modifier resins employed in the present invention are either branched polyethylene resins (described below) or copolymers of ethylene with 0.5—25 percent by weight of an α,β-ethylenically unsaturated carboxylic acid (also described below). When percentages of these modifier resins are referred to herein, weight percentages of the entire resin blend are intended, unless otherwise indicated.

The improved friction weldability can be

[*Price 5s. 0d.*]

expressed in terms of "percent joint efficiency", i.e.,

$$\frac{\text{lb. break load of welded joint}}{\text{lb. break load of original strap}} \times 100$$

For polyamide strapping wherein no other polymeric component is present, the joint efficiency is about 40 percent. When about 0.75 percent by weight of ethylene/acid copolymer is present in the strapping as a blend with the polyamide resin, a maximum improvement appears to occur, providing a joint efficiency of 55 percent and higher, preferably 58 percent. As the proportion of copolymer is decreased or increased from 0.75 percent by weight, the joint efficiency declines. Below 0.3 percent and above 5 percent by weight of copolymer, said improvement is negligible.

The ethylene/acid copolymer component of the strapping according to one embodiment of the present invention, a copolymer of ethylene with from 0.5—25 percent by weight of an α,β-monoethylenically unsaturated carboxylic acid, has a number-average molecular weight of at least 10,000 (measured by osmometry). The copolymer employed usually will have a melt index of between 0.1 and 100. The copolymer is made by copolymerizing ethylene and carboxylic acid, preferably following the procedure of British Patent No. 963,380, to give a copolymer in which the acid derived units are randomly distributed along the copolymer chain. The carboxylic acid monomer need not be in the acid form but can be in a form which yields the acid function in the copolymer chain. Preferably, the carboxylic acid has up to 8 carbon atoms, i.e. from 3 to 8 carbon atoms. Suitable acids include mono- and di- carboxylic acids, including compounds convertible thereto in the copolymer chain, such as acrylic, methacrylic, maleic and fumaric acids and the monoalkyl esters and the anhydrides thereof. The preferred copolymer is of ethylene and from 2—10 mole percent of methacrylic acid. The copolymer can include from 0.01—10 percent of the third ethylenically unsaturated monomers disclosed in U.S. Patent No. 3,201,734 to Simms.

The present invention will be discussed more fully hereinafter with respect to the drawings in which:

FIG. 1 shows in side elevation, strapping of the present invention in operative position for friction welding;

FIG. 2 shows an enlarged view of the overlapped portion of the strapping shown in FIG. 1 and the machine jaws gripping this portion;

FIG. 3 shows the relative oscillation of the jaws shown in FIG. 2 to obtain friction welding of the overlapped portions of the strapping;

FIG. 4 shows the strapping with the friction weld completed and the jaws removed; and

FIG. 5 shows the effect of ethylene/acid copolymer content on joint efficiency of the friction weld.

With respect to the drawings, FIG. 1 shows strapping 2 of the present invention tensioned around an article 4 to be strapped and having one end 6 overlapped with the opposite end 8 which continues onto a reel (not shown). The overlapping ends 6 and 8 are gripped between a pair of jaws 10 and 12 which press the overlapping ends together. These jaws are part of a machine 14, which can be, but is not limited to, the tool described in the Signode publication hereinbefore described, shown in phantom lines, which accomplishes the friction weld. The machine 14 can be equipped, for example, with a lever mechanism 16 for tightening the strapping around the article 4, a line 18 for compressed air for powering the machine, and a lever mechanism 20 for actuating the machine.

As shown in greater detail in FIG. 2, the jaws 10 and 12 have ridged or otherwise roughened surfaces 22 gripping the opposing faces of ends 6 and 8 of the strapping. Longitudinal oscillation of jaw 10 shown by the phantom line positions in FIG. 3 causes the strapping end 8 to move longitudinally and to repeatedly rub the mating surface of the strapping end 6 which is held stationary by jaw 12. The friction existing between these contiguous surfaces heats and eventually melts the strapping at these surfaces, causing them to weld together, as indicated by the weld line 24 shown in FIG. 4, when the longitudinal oscillation of jaw 10 is stopped. The low thermal conductivity of the strapping confines the melting to the surfaces being rubbed, thereby retaining the orientation in the main body of the strapping.

The present invention is not limited to any particular operating conditions insofar as obtaining the friction weld is concerned. The gripping pressure and amplitude and duration of rubbing are selected to accomplish the desired result. Representative conditions are given in the Signode publication hereinbefore described and in the Examples herein.

The best improvement in friction weldability occurs for strapping of blends containing about 0.75 percent by weight of the ethylene/acid copolymer. As shown by the curve in FIG. 5, the joint efficiency of the strapping increases from 40 percent with increasing copolymer content up to about 0.75 percent by weight, and at higher contents the joint efficiency decreases. Some improvement is obtained with as little as 0.3 percent by weight copolymer. A similar improvement is obtained with as high as 5.0 percent by weight. These values encompass the useful range of copolymer content insofar as improved friction weldability is concerned. Preferably, a joint

efficiency of at least 50 percent is desired, which is obtained at 0.5 percent by weight copolymer content. More improvement occurs in selecting contents along the curve between 0.5 percent and its peak. Compositions lying along the opposite side of the peak of the curve offer no advantage. From 0.5—0.95 percent by weight of copolymer encompasses an even more preferred range.

Turning now to the embodiment of this invention wherein branched polyethylene resins are employed as the modifier resin in this invention, the amount of branched polyethylene resin required will range from 0.2—3.0 percent by weight based on the weight of the resultant blend when improved friction weldability is desired. Higher amounts tend to decrease the friction weldability of the oriented article. When friction welding is not to be applied to the oriented article, e.g., its ends are complementarily beveled and fastened together with adhesive so as to be useful as power transmission belting, up to 5.0 percent by weight of the branched polyethylene can be present. For either type application, amounts smaller than 0.2 percent by weight do not show any significant improvement, and from 0.5—2.0 percent by weight of branched polyethylene resin is preferred.

The branched polyethylene resin is a well-known article of commerce. It is frequently called low density polyethylene, with the density being from 0.900 to 0.935 g/cc. measured according to ASTM D—792. It is desirable that the branched polyethylene resin have sufficient molecular weight to be tough; a melt index from 0.2 to 2.0, measured according to ASTM D—1238, is preferred. Linear or high density polyethylene resin has a detrimental effect on properties of the oriented polyamide article.

Referring to the use of either modifier resin of this invention in the manufacture of *strapping*, it is generally desirable that the resin blend be colored. This can be accomplished by blending the polyamide resin, modifier resin, and colorant together before fabrication into the ribbon shape and orientation thereof. The amount of colorant employed will depend on the colorant used and the particular color intensity desired. Carbon black is the colorant most often used. In a preferred embodiment, the colorant and modifier resin are pre-blended to form a color concentrate and sufficient of this concentrate is then blended with the polyamide resin to supply the modifier resin component of the blend.

The amount of colorant present in the concentrate will be in the range 5—60 percent by weight based on the weight of the concentrate, the exact amount being dependent on the dispersibility of the colorant in the modifier resin and on the intensity of color desired. Generally, sufficient colorant to opacify the polyamide strapping is desired. From 0.1—0.5 per cent by weight of colorant based on the weight of the blend is usually satisfactory; higher amounts can be used, e.g., up to 2.0 percent by weight can be used to improve weatherability.

The resin blends of this invention can be prepared by conventional methods. For example, color (or additive) concentrates can be prepared by mixing together colorant and modifier resin in a Banbury mixer or on a two-roll mixer at temperatures of about 150°C. for a sufficient time to obtain uniform dispersion. The concentrate can then be comminuted into granules of convenient size for either dry or melt blending with polyamide resin. The same technique can be used for blending modifier resin without colorant with polyamide resin. The melt blend can either be extruded into the ribbon shape for orientation or the extrudate can be comminuted into granules for re-extrusion or molding by other methods. The ribbon shape is preferably made by the molding process disclosed in Belgian Patent No. 701,558, granted January 19, 1968 to Fields and Hartig or by the extrusion process disclosed in Us. Patent No. 3,354,023.

The present invention is not limited to any particular method of accomplishing longitudinal orientation of the object made from the resin blends. The preferred orientation, however, is the roll oriented disclosed in British Patent No 1,017,175. Other methods of orientation such as stretching and die drawing can be used individually or in combination with each other or with roll orientation. In any event, the degree of longitudinal orientation is generally sufficient so that the oriented article has a tensile strength of at least 2,110 kg/sq. cm (3,515 kg/sq. cm where the modifier resin is the copolymer) measured on a conventional test machine. This corresponds to a deformation ratio of at least about 3 or 4 (weight per unit length before orientation divided weight of same length after orientation) for polyethylene-and copolymer-modified polyamide, respectively. Generally, for use as the power transmission belting, the tensile strength is 2,812—3,865 kg/sq. cm. For use as strapping, the tensile strength of the oriented article is generally greater than 3,865 kg/sq. cm.

Dimensions of the oriented article for use in power transmission belting are generally as follows: thickness at least 0.006 inch and most often between 0.038 cm and 0.076 cm; width at least 1.27 cm and most often between 5 cm and 10 cm. For definition purposes, "power transmission belting" is used herein to refer to the oriented polyamide article by itself instead of as a layer thereof laminated to a wear surface material such as leather or polyurethane. For strapping, the oriented article will have a thickness of greater than 0.025 cm and width generally between 0.63 cm and 1.89 cm.

In the following examples parts and percentages are by weight and weight percentages are based on total weights unless otherwise indicated. The melt indices, densities, and tensile strengths are determined under the conditions and procedures of ASTM Method D—1238, D—792, and D—638 (modified), respectively.

EXAMPLES 1 TO 3.

A control oriented article is made as follows: polyhexamethylene adipamide having a relative viscosity of about 50 (determined in accordance with ASTM D—789) and containing carbon black is extruded in the form of a ribbon which is then roll-oriented and stretched in accordance with British Patent No. 1,017,175 to produce an oriented article having a deformation ratio of about 4.3 and having a cross-section of 1.27 by 0.05 cm.

Additional oriented articles of the same dimensions are made using the same degree of roll-orientation and the same polyamide resin but containing branched polyethylene modifier resin. The polyamide resin containing the carbon black is melt blended with branched polyethylene resin and the resultant blend is extruded, cooled and comminuted into granules which are re-extruded into a ribbon and roll oriented. Additional details on composition and test results are given in Table I.

TABLE I

Example	Polyethylene In Blend wt %	Melt Index	Density g/cc.	Carbon Black wt %	Tensile Strength kg/cm²
1	0	—	—	0.125	5,000
2	1.8	0.25	0.919	0.125	4,680
3	0.9	0.25	0.919	0.125	4,750

The oriented articles of these examples are useful as strapping. When used for this purpose and the ends of the strapping friction welded together, the strapping of Example 1 has a joint strength (strength of bond) of 107 kg, whereas the strapping of Examples 2 and 3 have joint strengths of 172 kg and 140 kg, respectively. The friction weld is obtained using a commercially available friction welding tool described in the Signode publication operation at 6000 strokes/min. and 7 kg/sq. cm.

EXAMPLE 4.

Example 2 is duplicated except that the carbon black content is increased to 0.46 percent and the polyamide resin containing the carbon black and the polyethylene resin ingredients are first dry blended and then extruded to the ribbon shape. The tensile strength of the strapping is 4,670 kg/sq. cm and the friction-welded joint strength is 177 kkg.

EXAMPLES 5 TO 8.

The same blending procedure as Example 4 is followed for these examples to make strapping of the same orientation and polyamide resin, but unpigmented, as Examples 1 to 3, except that the branched polyethylene resin and carbon black and other ingredients are pre-blended, melt extruded and comminuted into granules. The polyethylene content and carbon black content in the polyamide resin is varied by varying the amount of pre-blend or concentrate blended therewith. The concentrate consists of 20 percent carbon black, 78.8 percent branched polyethylene, 0.4 percent $BaCo_3$, and 0.8 percent of an antioxidant available as Santonox AO—3. Further details and test results for these examples are found in Table II.

TABLE II

Example	Polyethylene In Blend wt %	Melt Index	Density g/cc.	Carbon Black wt %	Tensile Strength kg/sq. cm
5	1.75	0.24	0.917	0.44	4,630
6	1.10	0.24	0.917	0.28	4,560
7	0.32	0.24	0.917	0.08	4,707
8	0.28	0.24	0.917	0.07	4,830

A control strapping is made containing the same polyamide resin with 0.125 percent of carbon black and no branched polyethylene resin. This strapping has a tensile strength of 4,820 kg/sq. cm and a joint strength of 104 kg. The friction weld joint strength of the strapping of Examples 5, 6, 7 and 8 are 156, 145, 143 and 130 kg, respectively.

When the oriented articles of the foregoing examples are used in the manner of power transmission belting, they exhibit greater resistance to delamination than belting made from the control articles.

EXAMPLES 9 TO 14.

Example 9 is a control made by blending 15 parts of unpigmented polyhexamethylene adipamide having a relative viscosity of 50 as measured by ASTM Test D—789 with one part of the same polyamide containing 2 percent carbon. Example 10 was made with a concentrate containing 59.5 percent of a copolymer of ethylene with 9 percent methacrylic acid having a melt index of 4.0, 40 percent SRF—S furnace black, and 0.5 percent Santonox AO—3 antioxidant. Examples 11 to 14 were made with a concentrate containing 79.5 percent of the same copolymer used in Example 10, 20 percent SRF—S furnace black, and 0.5 percent of Santonox AO—3 antioxidant. The remainder of the blend for Examples 11 to 14 was polyhexamethylene adipamide. Strapping is prepared from these blends by extrusion of the blend into ribbon form which is roll oriented in accordance with U.S. Patent No. 3,354,023 to a deformation ratio of about 4.3. The friction weld is obtained using the tool described in the Signode publication, operating at a pressure about 35 kg/sq. cm, oscillating parallel to the length of the strap at an amplitude of 0.13 cm at 6000 cycles/min. for one-half to 4 seconds. The contact area between overlapping strapping ends between the jaws of the tool is 2.54 cm in length times the width of the strap. The breaking load in kilograms of the weld and of the strapping, for determining joint efficiency, is determined using an Instron (trademark) tensile tester using a cross-head speed of 5.08 cm/min. Further details and test results for these Examples are given in Table III.

TABLE III

Example No.	Per Cent Ethylene/ Acid Copolymer	Strap Dimensions Thickness, Cm	Width, Cm	Strap Tensile Strength, Kg/Sq. Cm.	Friction-Weld Joint Strength, Kg Force	Joint Efficiency Per Cent
9	None	0.0412	1.107	4,830	89	40
10	0.3	0.0419	1.118	4,720	96	43
11	0.50	0.0410	1.107	4,615	105	50
12	0.75	0.0417	1.110	4,608	127	60
13	0.95	0.0421	1.107	4,430	110	53
14	2.00	0.0415	1.105	4,295	93	46

WHAT WE CLAIM IS:—

1. An article formed of a molecularly oriented resin blend comprising a polyamide resin and from 0.2 to 5%, based on the weight of the blend, of a branched polyethylene resin.

2. An article according to claim 1, in which the resin blend contains from 0.2 to 3% by weight of the branched polyethylene resin.

3. An article according to claim 2, in which the resin blend contains from 0.5 to 2.0% by weight of the branched polyethylene resin.

4. An article according to any of claims 1 to 3, in the form of strapping.

5. An article according to any of claims 1 to 3, in the form of power transmission belting.

6. An article according to claim 1, substantially as herein described in any of Examples 2 to 8.

7. A modification of an article according to claim 1, in which the resin blend comprises a polyamide resin and from 0.3 to 5%, based on the weight of the blend, of a copolymer comprising units derived from ethylene and units derived from an α,β-ethylenically unsaturated carboxylic acid, the copolymer containing from 0.5 to 25% by weight of units derived from said acid.

8. An article according to claim 7, in which the α,β-ethylenically unsaturated carboxylic acid contains up to 8 carbon atoms.

9. An article according to claim 7 or 8, in which the resin blend contains from 0.5 to 0.95% by weight of a copolymer of ethylene and methacrylic acid, the copolymer containing from 2 to 10 mole percent of units derived from methacrylic acid.

10. An article according to any of claims 7 to 9, in the form of strapping.

11. An article according to any of claims 7 to 9, in the form of power transmission belting.

12. An article formed of a molecularly oriented resin blend, substantially as herein described in any of Examples 10 to 14.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

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2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

Fig. 1.

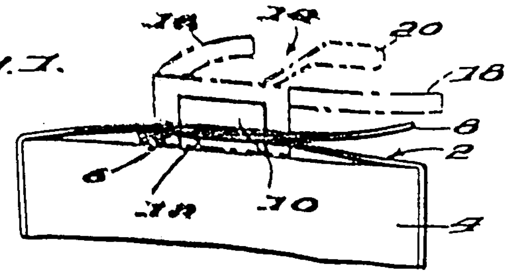


Fig. 2.

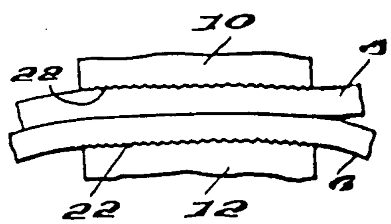


Fig. 3.

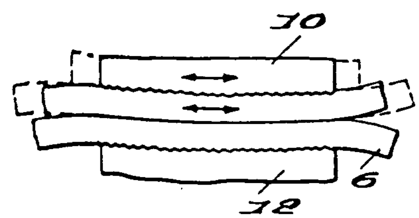
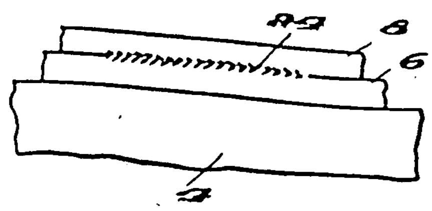


Fig. 4.



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Sheet 2

Fig. 5.